1936

Changes in the oxidation-reduction equilibrium in soils as related to the physical properties of the soil and the growth of rice

Madison B. Sturgis

JANUARY, 1936 LOUISIANA BULLETIN No. 271

Changes in the Oxidation-Reduction Equilibrium in Soils as Related to the Physical Properties of the Soil and the Growth of Rice

By
M. B. STURGIS

LOUISIANA STATE UNIVERSITY
AND
AGRICULTURAL AND MECHANICAL COLLEGE
AGRICULTURAL EXPERIMENT STATIONS

C. T. DOWELL
Director

CONTENTS

CHANGES IN THE OXIDATION-REDUCTION EQUILIBRIUM IN SOILS AS RELATED TO THE PHYSICAL PROPERTIES OF THE SOIL AND THE GROWTH OF RICE*

By M. B. STURGIS

Observations made during the past five years in studies on the fertility problems of the soils of the lower Mississippi flood plain and the soils of the coastal prairies which are southwest of and adjacent to the alluvial soils show that the development of reducing conditions both from naturally poor drainage and from irrigation gives rise to peculiar difficulties. In the study of organic decomposition and nitrification in Sharkey soils which are the most extensive first bottom soils along the lower Mississippi, it was noted that the retardation and lag in the micro-biological processes following seepage from the river during the spring rises indicated that some factors which are toxic or inhibitive to bacterial action in the soil develop during poor drainage and disappear relatively slowly following drainage. Similar conditions prevail following the growing of rice which has been irrigated by methods where the soil is kept submerged from the time the rice is six inches high until the crop is almost mature. Especially has it been recognized that after rice has been grown on Crowley soils, upland crops do not usually make satisfactory growth from plantings immediately following the rice. The long continued practice of irrigation causes the development of deflocculation and other poor physical conditions in these soils and also tends apparently to permit the accumulation of reduced products which may become inhibitory or toxic to crops.

Since the effects of irrigation or water-logging on the intensity and products of reduction and their relation to the physical properties of the soil and the growth of rice have not been previously isolated or quantitatively determined, such studies are of both scientific and economic interest. The object of this investigation has been to determine the effect of water-logging and organic matter on the rate, intensity, and amount of reduction, to study the effects of irrigation on the decrease in permeability and aeration, and to ascertain the effects of certain treatments on the improvement of the physical properties and the growth of rice in Sharkey and Crowley soils.

HISTORICAL

Studies conducted by the author (50)** on the decomposition of sugarcane trash in soils of the same series as those used in this investigation have shown that when the moisture conditions and aeration of the soil are kept at optimum, the decomposition is rapid and the depression of the available nitrogen of relatively short duration.

*Submitted as a thesis in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State College.

**Numbers in parentheses refer to "Literature Cited."

However, under intermittent high moisture conditions, the decomposition was slower and the depressive effects on the available nitrogen could not be corrected by means of additions of commercial nitrogen. The extremely low rate of nitrification in the spring following poor drainage through late winter and early spring cannot be accounted for solely through low temperature and high moisture content. There appeared to be some toxic factors which developed under wet conditions and disappeared relatively slowly when the better drainage and higher temperature prevailed. These toxic factors persisted sufficiently to materially lower the yields of corn.

Gillispie (22) found that soils became highly reducing when treated with an excess of water and that the intensity of reduction could be measured by the determination of the reducing potentials. The intensity of the reduction developed in a submerged soil is increased by the presence of decomposable organic matter. The addition of 0.1 per cent of glucose to water-logged soil caused a very pronounced reducing condition.

Clark (15) after extensive experiments supported the main features of Gillispie's work in regard to the use of the electrode in following the course and intensity of reduction in cell suspensions. He very carefully pointed to the fact that the processes of oxidation-reduction are not reversible as in many dye and inorganic systems. Poising is slow and the activity of partially cytolyzed cells induces a continuous change in the electrode potential. He found also that Eh potentials are never more positive than about 0.2 at pH 7.0, even when air has been bubbled through the cell suspensions. On the other hand, cultures of certain anaerobic bacteria cannot only induce the potential of the hydrogen electrode, which is the reference electrode having an Eh value of 0 at pH 0, but also a slight overvoltage or negative Eh value.

Cannan, Cohen, and Clark (13) have shown that the measurement of the potential differences at unattackable electrodes immersed in cell suspensions can be used to follow the progress of reducing intensities in the presence and absence of indicators. There can be found a definite potential difference between an electrode and a solution containing a mixture of oxidant and reductant. This difference is a function of the ratio of oxidant to reductant and of the pH of the solution. The characteristic potentials of a system indicate quantitatively its oxidizing or reducing relation to other systems. In contrast to solutions, cell suspensions are poorly poised with respect to the electromotively active material present at any moment but active material is slowly mobilized by cell catalysts from some large reserve. Electrodes in cell suspensions act as in solutions containing systems intermediate between those which poise well and those which have no definite effect.

In the works cited (15, 13, 54, 4) and other more common sources, the theoretical mechanisms for and the importance of oxidation-reduction reactions have been generally in agreement. Oxidation is the process in which ions, atoms or substances give up negative electrons with the liberation of definite quanties of energy. Reduction is the process in which ions, atoms or substances take on electrons. All electro-chemical changes involve oxidation and reduction. In the combination of atmospheric oxygen with substances with the liberation of energy, the molecular oxygen is reduced. During the formation of water, hydrogen atoms lose negative electrons and are oxidized while oxygen atoms receive the electrons and are reduced. Through the addition of an electron, e, there is a storage or release of a quantum of energy. The process of photosynthesis brings about the transformation of light energy into chemical energy by the reduction of carbon and hydrogen. In respiration the stored energy is changed to kinetic energy or heat by the hydrogen and carbon atoms losing electrons and becoming more positive, while the oxygen atoms receive electrons and become more negative.

The respiration processes associated with the cell tend to liberate energy so that if one atom is reduced another must be oxidized with an equal or greater liberation of energy than was required for the reduction. The significance of this fact is that normal respiration in the soil is predominantly aerobic and unless free oxygen is available during organic decomposition, the highly reactive nascent fragments of sugars and other organic substances, which have unsaturated valences, tend to combine with the oxygen of nitrates, sulphates, ferric compounds, etc., or to liberate energy through the oxidation of part of the molecule at the expense of the remainder. The amount of energy liberated in the oxidation of organic substances by oxygen that has been obtained through the reduction of other compounds is only a fraction of the amount that could have been obtained through the oxidation with free oxygen. Under very reducing conditions most of the energy liberated in the formation of carbon dioxide must be consumed in the production of highly reduced products as hydrogen, methane, butyric acid, etc. Commonly the reduced products, especially soluble sulfides and ferrous compounds, may be toxic to plants and to beneficial bacteria and, although the reduced products which have accumulated are oxidized with the evolution of energy when the soil is aerated, the energy liberated in their oxidation is probably not efficiently used in any of the more important biochemical processes of the soil.

Willis (54) and Bradfield and others (4) have found that the determination of the actual potential existing in a soil at any given time is a difficult procedure. The soil is very heterogeneous and contains many oxidants and reductants or many more or less distinct oxidation reduction systems.

It is only with reservations that the standard formulas for oxidation-reduction equilibriums could be considered as applicable to systems in the soil. However, the potentials observed in well aerated soils appear to be dominated by the inorganic ferrous-ferric iron system and, at least, the general oxidation-reduction equations might be assumed to apply for the purpose of illustration. If a platinum wire as an electrode is placed into a solution it will take on a potential which is a function of the ratio of oxidant to reductant in the solution. Reducing ions tend to give up electrons to the electrode and make it more negative as they become oxidized. Oxidizing ions tend to take electrons from the electrode and leave it more positively charged as they are reduced. The potential developed in a solution can be determined by an ordinary potentiometric set-up and, by reference to the value that would have been developed against the normal hydrogen electrode which has been assigned a standard value of Eh equals 0, it can be compared with the potentials of other solutions. The relation of the potential of an oxidation-reduction equilibrium to the potential of the standard hydrogen electrode at pH 0 is expressed by the following equation:

$$Eh = Eo - \frac{RT}{nF} \ln \frac{(Red)}{(Ox)}$$

Where Eh is the difference between the platinum electrode and the normal hydrogen electrode, Eo is a constant characteristic of the particular equilibrium, R is the gas constant, T is the absolute temperature, n the number of charges concerned, F the farad, Red is the molar concentration of reductant and Ox is the molar concentration of oxidant. The equation given above applies only to conditions at pH 0. At a temperature of 30° it may be shown that for each unit increase in pH there is a decrease of 0.06 volt in Eh. If hydrogen is being evolved in a solution in which is immersed a platinum electrode, the platinum surface will become saturated with hydrogen and act as a hydrogen electrode. The hydrogen absorbed on the electrode is then in equilibrium with the hydrogen ion, H+, in the solution and with the hydrogen in the atomic condition, H. The pressure, P, under which the hydrogen is evolved is a function of the H+ and H concentrations in the solution. Substances in the solution may then react with either hydrogen ions or water to liberate gaseous hydrogen and build upon the electrode a definite hydrogen pressure, or the reverse may occur. The hydrogen on the electrode may go into solution and cause the reduction of substances in the solution. Then, if a constant pressure of hydrogen gas is maintained at an electrode in equilibrium with a solution at a known pH, the potential at the electrode may be used as a measure of the Eh and refers to the potential produced by a definite pressure of hydrogen. The relationship is expressed by the general equation:

$$Eh = EH - \frac{RT}{nF} \ln \frac{\sqrt{P}}{(H+)}$$

In a similar manner, Willis (54) has shown the relationship between Eh, pH, and oxygen pressure. His calculations show that under equilibrium conditions the intensity of oxidation should vary inversely with pH and directly with the logarithm of the oxygen pressure. On the basis of assumptions from the result of theoretical calculation the indication is that in the soil the effect of changes in the pH on the activity of oxygen should be very great, relative to the effect of changes in oxygen pressure. If equilibrium conditions could actually exist in the soil, an increase in pH could be considered as equivalent to a decrease in the activity of oxygen, but microrganisms are constantly using the oxygen, and the rate of supply of oxygen is a dominant factor. Willis found that soil suspensions are weakly poised and that there is generally a drift to the negative. Particularly was a pronounced negative drift noted in deaerated suspensions. The drift is due largely to the production of low potential material and to the depletion of oxygen. Also the drift was found to be most rapid at high pH values. Earlier work of Willis (53) suggested that the effect of the hydrogen-ion concentration on the oxidation-reduction equilibrium might be of more significance than the pH alone. In the case of the humus fraction of a peat soil, it was found that organic matter constituted an oxidation-reduction system from which the curve showing the relation of Eh to pH had a slope of—0.06 in the acid range and a zero slope in the alkaline range. Willis states that well aerated soils low in organic matter would be expected to exhibit oxygen potentials but that on the removal of free oxygen other components as iron compounds might maintain the established potential. He concludes that aerobic or anaerobic conditions cannot be defined by soil potentials.

Remezov (43) from studies on the changes of the oxidation-reduction potential in podsolised soils observed that under different degrees of swampiness the Eh varied from 11 to 353 millivolts and that the lower Eh was associated with the stronger swampiness. The determination of the potential was attended with difficulty as the potential varied greatly with time.

Bradfield and others (4) have found that measurements of the oxidation-reduction potential in soils promise to be a more useful index of subsoil drainage over a longer period of time than groundwater observations. The determinations of the potential were made in suspensions of the soil in 0.1 N sulphuric acid. By lowering the pH the concentration of the ions of the oxidation-reduction system is greatly increased and the ratio between them is not so easily disturbed, or the system is better poised. These workers observed that a change of 0.08 volt per unit change in pH fit their conditions better than the theoretical value of 0.06 volt. The experimental error in the determination of the potential was accepted as approximately 10 millivolts.

Kohnke and Bradfield (35) have concluded that particular difficulty is met with in determining the oxidation-reduction potential in soils due to the oxidizable and reducible components that occur in the colloidal state. The aqueous suspensions of these materials are not stable. The factors which influence the more permanent changes in the potential are the degree of saturation with water, temperature and the nature and amount of organic compounds present.

Robinson (44) studied the effects of submergence on a number of widely different soils and found that reducing conditions may develop within eight days. Toxicity in submerged soils is due largely to soluble iron, soluble manganese, and hydrogen sulphide or to a general reducing condition, which in itself is the main and most toxic agent. Robinson stated that the carbon dioxide produced by the microbiological decomposition of organic matter is mainly responsible for holding the iron and manganese in solution. The solubility of iron sulphide is also increased by the production of carbon dioxide. Robinson stated from the work of others that most upland crops will not tolerate more than 5 parts per million of ferrous iron in solution.

Brenchley (6) found that 2.5 parts per million of manganese in solution was toxic to peas, while barley would endure 10 parts per million. She also found that iron is antagonistic to manganese.

An increase in acidity or reduction increases the solubility of iron and manganese. McGeorge (39) observed that all soils in which the acidity was higher than pH 5.8 contained soluble salts of iron, aluminum and manganese. At pH 6.0 or above, manganese was not present in the soil solution and iron and aluminum were present only as hydrosols. Conner (16) found manganese and iron apparently to have been largely reduced and made soluble by saturating the soil with water. Unlike the iron the manganese did not rapidly oxidize in air-drying the soil.

According to Piper (41) the two forms of manganese in the soil that are important as a source of manganese for plants are replaceable bivalent manganese and manganese dioxide. The relative amount of these two forms is controlled by the soil reaction and the oxidation-reduction equilibrium. The availability of manganese is influenced by these two factors acting together. Manganese has been found to have been reduced and rendered soluble in water-logged soils as alkaline as pH 8.0. Soil conditions that favor reduction processes have been shown to increase the amount of manganese available to the crop.

Halvorson (23) has shown by calculation how the lowering of the pH or the oxidation-reduction potential will increase the amount of ferrous iron remaining in solution. Solutions in which bacteria are growing even under aerobic conditions favor the solution and reduction of ferric iron especially if the solution becomes acid.

Under anaerobic conditions heterotrophic microorganisms dissolve and reduce ferric hydroxide. The changes result from decrease in oxygen pressure and formation of acid and may occur at reactions close to neutrality. The effect of heterotrophic bacteria on the solution of iron is very important on account of the fact that they can induce changes favoring solution which do not occur spontaneously.

Harrison and Aiyer (24) observed that the gaseous products of the decomposition of organic matter in flooded rice soils consisted chiefly of methane, smaller proportions of nitrogen, carbon dioxide and hydrogen. The gases evolved from the surface of the soil consist mainly of oxygen and nitrogen. The nitrogen evolved from the immediate surface of the soil is derived largely from the atmosphere by a purely physical reaction. The absence of carbon dioxide and hydrogen from the gases evolved from the surface of the flooded rice soils was later accounted for by the fact that bacterial action takes place resulting in the reduction of the carbon dioxide by the hydrogen and the formation of organic matter or methane (26).

Harrison and Aiyer (25) have shown that the relationship between gas production in rice soils and oxygen evolution by the algal film at the immediate surface is due to symbiotic interchanges between the microorganisms found in the film. Methane and any hydrogen which reach the surface are oxidized with the production of carbon dioxide and water. The carbon dioxide is then decomposed largely by algae with the evolution of oxygen. Also, there appear to be present autotrophic microorganisms which assimilate carbon dioxide and methane to produce organic matter that may be utilized by the organisms which are responsible for the oxidation processes. The oxygen liberated at the surface of the soil is dissolved in the water entering the soil and is utilized for root aeration. The aeration of a flooded rice field depends on the rate of organic decomposition or the production of the gases, particularly methane, hydrogen and carbon dioxide, on the activity of the surface film, and on the permeability of the soil to the downward movement of the water charged with a high concentration of dissolved oxygen. In very impermeable soils, it was found that, due to the inability of oxygenated water to penetrate the soil, root growth was restricted to the very top of the soil and stunted plants and poor crops were produced.

The root-rot of rice, "mentek," in Java is a disease or condition in which the root is incapacitated to supply the plant with nutrients and water and is caused by the lack of oxygen in the soil and consequent accumulation of reducing substances about the roots. Van der Elst, according to Copeland (17), has proven the relationship of lack of aeration to development of the disease. He found that in water cultures where the oxygen was excluded from the water some symptoms of root-rot appeared within two days. When 100 parts per million of ferrous sulphate was added to the culture solutions, typical

symptoms of "mentek" were produced within one day. In practical rice culture the root-rot occurs exclusively in irrigated rice fields and is found in infertile shallow soils which have poor structure and imperfect drainage.

Bonazzi (3) has found that the primary roots of rice are obligate aerobic organs and that under the conditions of anaerobic germination toxic substances, hydroxy acids of the lactic acid type, alcohol and acetone, accumulate in rice seedlings. Among the products of anaerobic germination of rice there are some, especially the hydroxy acids, that have a toxic action for the development of the radicle in new plantings made in the presence of oxygen. Studies on the reduction of nitrates under aseptic conditions by extracts from macerated rice plants indicated that there exists in rice plants a very active reducing mechanism.

Jones (32) in studying the effect of continuous submergence on the germination of rice in soil found that if the rice seed were placed one inch or deeper into clayey soils and the soils kept continuously submerged, normal germination did not occur and 20 per cent or less seedlings developed. Apparently there was insufficient oxygen under such conditions to initiate the growth of the radicle. Results from germination of rice in pots into which oxygen was forced indicated that the lack of oxygen is the principal factor causing abnormal germination and seedling development when rice is planted to any appreciable depth in continuously submerged soils.

Cannon (14) from studies on the effects of varying the amounts of carbon dioxide and oxygen on the growth of rice seedlings in soil cultures through which the gases were forced observed that the roots of seedling rice are capable of maintaining growth in percentages of carbon dioxide up to 49 per cent and on the other hand that growth will go on, although slowly, in as little as 0.5 per cent oxygen, which indicates that rice is adaptable to poor aeration.

The full importance of concentration of carbon dioxide and of the diffusion of carbon dioxide and oxygen in flooded soils has not been extensively studied, but valuable inferences can be drawn from the results of studies on drained soils (48). Smith and Brown (49) found that the percentage of carbon dioxide in the soil air in cropped soils was much higher than in fallow soils. These workers also found that the carbon dioxide in soils was produced by the crop plants and by the microorganisms. They assumed a small amount to be produced by chemical action. Deep-rooted leguminous plants were found to produce more carbon dioxide than non-leguminous plants. There was an average percentage of 1.84 carbon dioxide in the soil air under alfalfa, 1.15 under corn, and 0.43 under fallow.

Buckingham (8) measured the rate of the diffusion of carbon dioxide, nitrogen and oxygen through partially moist soils and found

the rate of diffusion of the gases to be determined mainly by the total porosity of the soil, and that rate of diffusion was approximately proportional to the square of the porosity.

Keen (34) states that the rate of the diffusion of a gas through a soil depends mainly on the total free pore space and not to any great extent on the dimensions of the individual pores. Although Keen's equations apply only to the diffusion of gases through the free pore space in soils, he has suggested the importance of aeration by movement of water saturated with the gases. He has also pointed out the very important fact that minute pores would tend to be closed with water and especially would this effect be increased by colloidal materials that swell in water.

Buehrer (9) has shown that the relation between the structure constant and the porosity of soils is not simply linear, as would be expected if all pores were continuous for gas or liquid flow. Apparently a certain proportion of the channels is closed at one end and unless, through the action of roots or other agencies, these channels become continuous they do not contribute to the flow of either gases or liquids.

The importance of carbon dioxide in the absorption of the nutrients, particularly of phosphorus and potassium, has been described by workers in Arizona. Breazeale (5) has shown that plants can absorb the carbonate ion from soil carbonates, but he did not consider that the carbon absorbed through the root was of major importance in the photosynthetic process in the leaves. The absorption of the carbonate ion does not appear to take place unless some soluble base is present. Breazeale concluded that the plant probably absorbs the carbonate ion or exudes carbon dioxide for the purpose of maintaining equilibrium in its tissues or in the solution in which it is growing. Buehrer (10) has pointed out that the $^{-}H_2PO_4$ is the phosphate ion likely to be in greatest abundance within the range in reaction where phosphate absorption by the plant is optimum and must be the ion upon which the plant largely feeds. If the phosphate ion is not present in this form, the plant can make the the conversion by the exudation of carbon dioxide. McGeorge (40) has found that phosphate absorption by the plant is most active between pH 5.5 and 6.8, and expressed the view that there can be no absorption of phosphate from a calcareous soil in the absence of carbon dioxide. In soils very low in organic matter the exudation of carbon dioxide from plant roots is the main source. Where the rate of diffusion of carbon dioxide is restricted as in the case of puddled soils, the exudation of carbon dioxide may become toxic due to slow, outward diffusion of carbon dioxide and slow, inward diffusion of oxygen. A certain balance between carbon dioxide and oxygen must exist. Demonstrations in water cultures have indicated that there is no absorption of phosphate in an excess of carbon dioxide. McGeorge concluded that

the proper balance between carbon dioxide and oxygen is impossible in puddled soil because of restricted diffusion of carbon dioxide and oxygen.

Russell (46) has summarized the evidence regarding the losses of nitrogen from soil and drawn the conclusion that there is no clear proof of the total loss of soil nitrogen by denitrification in soils under natural conditions or even in soils which have been temporarily water-logged. However, the loss of nitrogen by denitrification through bacterial action on decomposable organic matter under anaerobic conditions in soil cultures has been demonstrated.

Leather (36) determined the composition of gases from swamp rice soils. The amount of nitrogen evolved from plots of manured and unmanured soils showed that much greater quantities of nitrogen were evolved from the manured plots. It was inferred that part at least of the nitrogen was derived from the soil and green manure. Through a comparison of the ratio of nitrogen to argon, dissolved in water which had been shaken with air, to the ratio of the two gases present in rice land, Leather concluded that a high proportion of the nitrogen was derived from the soil and manure.

Kapp (33) found that the lack of nitrogen is responsible for most of the abnormal growth of rice on Crowley and Clarksville soils and that large applications of nitrogen in the forms of sodium nitrate and ammonium sulphate made every two weeks increased greatly the yields of rice under controlled conditions. Nitrogen was lost from the fertilized soil after submergence. Nitrates were lost more rapidly than ammonium forms. Nitrites did not accumulate in submerged soils in sufficient amounts to be toxic to rice. Nitrogen was not lost as ammonia. Kapp stated that the fertility of the soil must be maintained by a system which will increase the soil organic matter and which will allow the organic matter to partially decompose under aerobic conditions to insure the liberation of sufficient nitrogen after submerging.

Studies on the nature of the rice soils in the coastal prairies of Louisiana show that continuous flooding causes marked changes in the physical and chemical properties of these soils (18). The native characteristics of the soils are such that they tend to become compacted (28,18). The tendency toward deflocculation becomes especially marked as the soil organic matter is depleted from cropping and as irrigation is continued. In cases where salt water has been used in the irrigation of rice the soils have become more alkaline and deflocculation is most markedly developed.

An extensive review on the results from fertilizers on rice by the author (51) indicates that the continuous culture of irrigated rice on soils low in organic matter or through which water drains slowly causes the development of toxic or inhibitory conditions which

lower the yield of rice. Under the conditions of poor aeration the lowered oxygen supply in the soil and the accumulation of reduced substances slow up the decomposition processes of bacteria which liberate nitrogen from soil organic matter and cause the soluble phosphates to be changed to less available forms. After deflocculation, extremely poor drainage and the consequent poor aeration have developed in rice soils, the simple application of commercial fertilizers will not be effective, but by draining the land and turning under legumes the yields of rice may be increased.

The results of previous work and an analysis of data in the literature show that the decomposition of organic matter in waterlogged soils causes the accumulation of reduced products. The actual amounts of the reduced products that are likely to be toxic to irrigated rice have not been determined. Determination of the intensity of reduction or the oxidation-reduction potential in soils is attended with considerable difficulty and the results secured can be considered only as approximate values. It has been shown that the use of the oxidation-reduction potential as an index of aeration has serious limitations due to the fact that systems other than the oxygen system may maintain relatively high potentials. Data in the literature indicate that nitrogen may be lost from flooded soils and that the low availability of nitrogen to irrigated rice is a most serious difficulty. The aeration of a flooded soil depends on the downward diffusion of oxygen and on percolation carrying dissolved oxygen downward. There is no obvious mechanism to supply free oxygen in a deflocculated and impermeable soil under flooded conditions. The slow diffusion of carbon dioxide and oxygen on the accumulation of soluble ferrous iron in flooded soils, particularly if the soils were alkaline, would reduce the availability of phosphorus to very low values.

EXPERIMENTAL

Experimental Materials and Methods

The soil used in these experiments was taken from a very fertile area of Sharkey clay loam located on the farm of the Louisiana Agricultural Experiment Station at Baton Rouge and from areas of virgin and cultivated Crowley silt loam located on the Rice Experiment Station at Crowley.

The Sharkey clay loam is a very extensive Mississippi first bottom soil. The A horizon is dark-brown finely granular clay loam to a depth of 8 inches. The B horizon consists of a dark-drab to bluish clay, which is sticky and plastic when wet and very crumbly or coarsely granular when dry, extending to a depth of about 24 inches below the A. Below this is a yellowish plastic silty clay loam to a clay parent material.

Analyses were made on samples from the A and B horizons, but only soil taken as representative of the A horizon was used in the

pot tests. The agricultural history of the soil is not definitely known except that it has not been planted to rice within the last ten years during which time it has been in rotation of sugarcane, corn and soybeans. .

The Crowley silt loam soil is a coastal prairie soil. In the virgin state the A horizon consists of 6 inches of dark-gray friable finely granular silt loam which contains a few pockets of ashy siliceous material extending into the B. The B horizon extends from the A to a depth of 24 inches and consists of a brownish gray silt loam which has a granular to slightly columnar structure. The C horizon extends from below 24 inches and is a gray clay mottled brown and contains a small number of iron concretions.

The Crowley silt loam soil which has been used in these experiments and designated as deflocculated Crowley silt loam differs in physical properties from the virgin soil. The differences have been due to cropping the soil to irrigated rice over a period of forty-four years. The soil has not been planted to rice continuously but in general has been in rice two years and then out for one year. When it was kept out of rice, it was usually planted to soybeans or left fallow. The water used in the irrigation has been about neutral in reaction and has contained about 300 parts per million of soluble salts, of which about 60 parts per million was sodium. The irrigation water has been pumped from a deep well and its analysis shows it to be good water for irrigation. The profile of the deflocculated Crowley silt loam shows an A horizon having an average depth of 6 inches of gray silt loam which has a platy structure, brown iron stains around the channels of old roots, numerous iron concretions below 4 inches and numerous tongues of ashy gray siliceous material extending to depths of 20 inches or more into or through the lower horizon. The upper part of the B horizon from a depth of 6 to 15 inches is a light-gray streaked with brown silt loam having a compact coarsely granular structure. The lower B extends from a depth of 15 to 24 inches and consists of a purplish brown clay which has a very compacted blocky to columnar structure. Apparently the C horizon of the deflocculated soil is similar to the C of the virgin soil. Analyses were made on samples from the A, B, and C horizons of the virgin and on only the A and B horizons of the deflocculated soil. Soil from the A horizon was used in the lysimeter and pot tests.

The total analyses were made according to the method of the Bureau of Chemistry and Soils as proposed by Robinson (44).

The determination of the available nutrients was made according to the method of Reed and Sturgis (42). This method is based on the common procedure of determining exchangeable bases by the use of 0.05 N hydrochloric acid. The amounts of exchangeable or easily soluble bases have been considered as fair indices of availabilities of the basic ions (29, 30, 19, 21). The rate of increase in the solution

of phosphorus from a given weight of soil through increasing the proportion of 0.05 N hydrochloric acid to the sample was used as a measure of the availability of phosphorus.

Exchangeable hydrogen and the degree of saturation were determined by the use of barium acetate. This reagent was used on the basis of the fact that extensive tests had shown it to be very effective in replacing exchangeable hydrogen (52).

The pH was determined colorimetrically on clear soil extracts which were obtained by the use of the soil itself as a filter in a perforated test tube. The results from the colorimetric procedure were checked by the use of the hydrogen electrode.

The reducing capacity of the soil was determined by a procedure which was developed during the progress of the investigation. A 25-gram portion of the sample of moist soil which had just been taken from a depth of 5 inches was transferred immediately by washing with 25 milliliters of 0.1 N potassium dichromate and 100 milliliters of 0.5 potassium sulphate to an Erlenmeyer flask. The flask was stoppered and the soil and oxidizing solution shaken and allowed to stand for 2 hours. The solution was filtered off, a 25 milliliter aliquot taken and the excess potassium dichromate determined iodimetrically. After the potassium iodide was added, it was found necessary to titrate with the thiosulphate within five minutes. The amount of the dilution of the oxidizing solution by the soil moisture was calculated and the correction applied to the results which are given as the volume of 0.1 N potassium dichromate reduced per 10 grams of dry soil. The procedure is open to the criticism that some of the reduced organic compounds would not be oxidized and the less soluble inorganic substances would not be acted on. The relative high values obtained and the ease with which duplicates can be checked do, however, recommend its use in a comparative study.

The oxidation-reduction potential of the soil was determined in a manner similar to the procedure recommended by Allyn and Baldwin (1) and Brown (7). It was found that the use of a vacuum-tube potentiometer as recommended by Allyn and Baldwin was an unnecessary refinement in reading potentials in highly reducing soils due to a rapid negative drift which would not allow for determinations that could be checked more closely than 10 millivolts. The time consuming manipulation of Brown for seating the electrode in the soil could not be used in highly reducing soils because of the fact that any considerable exposure of the sample to the air may produce marked changes in the values obtained. The samples were taken as in the procedure described for the determination of the reducing capacity. Enough of the fresh sample to fill a small beaker to a depth of about an inch was covered with freshly distilled water and allowed to stand for 30 minutes. Then two heavy wire electrodes

of bright platinum which had been cleaned with nitric acid, washed and allowed to stand in distilled water were placed in the wet soil and contact made with a saturated calomel half-cell through an agar bridge and a potentiometric set-up. The e. m. f. was estimated first by making contact through one electrode and then by taking a final reading from the other within 10 minutes. Due to slow poising in soils which have been well aerated and to a rapid negative drift in soils which have become reducing, the values found and reported in volts are not considered significant beyond the second decimal. The data were corrected to the standard normal hydrogen electrode, by adding the value of the saturated calomel half-cell to the observed e. m. f. with the correct sign. The values are reported as Eh, without corrections having been applied for pH.

The soluble substances in the Sharkey soil were obtained by extracting the soil with water according to the Bureau of Soils method (47). The 1:5 water extract method could not be used on the Crowley soils because of the high degree of colloidal dispersion in the soil; so it was necessary to determine the soluble substances on the percolate secured by opening the bottoms of the pots and lysimeters periodically and collecting the percolate. Percolation was forced through the soil by keeping a head of fresh water on top of the soil. The bottoms of the pots and lysimeters contained a layer of acid-washed sand which permitted the maximum percolation that could be obtained under the conditions. Actually the percolate used in the analyses might be considered as a soil solution under saturated conditions which had been more or less displaced by water.

The fact that varying the ratio of soil to water causes variations in the amounts of the different ions, except the nitrate ion, present in the soil solution or water extracts of the soil (12, 11) does not permit an accurate comparison of the solubilities of the various ions present in the different soils.

The nitrates, nitrites, iron, manganese, aluminum, phosphorus and silica in the water extracts and percolates were determined by conventional colorimetric procedures.

Ammonia nitrogen was determined by replacing the ammonia with 0.5 N potassium chloride and then by distilling the ammonia over into standard acid and titrating it.

Soluble sodium was determined by the magnesium uranyl acetate method as outlined by Lemmermann (37).

All the determinations were made in duplicate and all the soil treatments were duplicated.

Experimental Results

The results of total analyses of the A and B horizons of the Sharkey clay loam are shown in table 1. It had been observed that

the soil was very high in available phosphorus (50) and that sulphides were readily produced after the soil had been water-logged for a few days. These conditions indicated that the soil was high in total phosphorus and sulphur. The analytical results show that the soil has a high phosphorus content, but the sulphur content is not so high as had been expected. It is relatively little higher in sulphur than other soils of the region (20). The data show that the B horizon has a higher nitrogen content than the A. This is a very significant condition. The higher content of nitrogen in the deeper horizon may be due to the effects of less aeration and lower temperature on the rate of organic decomposition.

Table 1.—Total analyses of the A and B horizons of Sharkey clay loam.

Constituents	Sharkey A	Sharkey B
SiO_2	72.00 %	62.70 %
TiO_2	0.25	0.33
Fe_2O_3	5.32	6.15
Al_2O_3	13.16	19.13
MnO	0.067	0.069
CaO	2.41	2.68
MgO	1.30	1.65
K_2O	0.86	0.97
Na_2O	0.85	0.69
P_2O_5	0.28	0.24
SO_3	0.12	0.08
Cl	0.028	0.025
Ignition Loss	4.15	5.22
N	0.108	0.119

The data in table 2 indicate that the Sharkey clay loam contains relatively large amounts of the exchangeable or easily soluble basic elements, and especially does it contain a large amount of easily soluble phosphorus. It can be seen from the data that, as the ratio of soil to the dilute acid used in extracting the phosphorus was decreased, there was a rapid increase in the amount of soluble phosphorus per unit weight of soil. Preliminary work had shown that it was not practical to carry the ratio of soil to 0.05 N hydrochloric acid to less than 1:100. It was also found that when this ratio of soil to acid was used all the phosphorus that could be dissolved by the acid was put in solution. The amount of phosphorus which is put into solution when the 1:100 ratio of soil to acid is used may be taken as an indication of the maximum amount of easily soluble or available phosphorus. It has been shown that soils which show 60 parts per million or more of soluble phosphorus by the method used contain sufficient phosphorus for normal crop growth (42). On a comparative basis the results show that the soil is very high in available phosphorus.

Table 2.—Available nutrients and degree of saturation in the A and B horizons of Sharkey clay loam.

	Sharkey A	Sharkey B
Total N %	0.108	0.119
Available K, p. p. m.	460	300
Available Ca, p. p. m.	4600	5020
Available Mg, p. p. m.	468	634
Available P, p. p. m.		
1:10 soil:acid	30	42
1:40 soil:acid	132	152
1:100 soil:acid	330	250
1:100 soil:H_2O	10	7
Exchangeable H, m. e. per 100 g.	0.68	0.68
Total exchange, m. e. per 100 g.	27.9	43.6
Degree of sat. %	97.6	98.4
pH	7.2	7.4

In order to arrive at quantitative determinations on the effects of organic matter and flooding on reduction, the accumulation of reduced substances, the solubility of phosphorus, and the changes in nitrogen, the Sharkey soil was treated in 3-gallon pots. One series of treatments, numbers 1 to 4 inclusive, was kept at 50 per cent of the moisture holding capacity. Another series, numbers 5 to 8, was kept saturated with water, but was not allowed to drain. The pots containing the soil were kept in a constant-temperature room at 30°. The treatments were as follows:

1. Check, untreated soil.

2. Soil to which was added soybeans. The whole plants were ground so as to pass a 2 mm. sieve, and used in an amount equivalent to 0.50 per cent organic matter and 0.0094 per cent nitrogen on the basis of the soil mixture.

3. Soil to which was added cane trash in an amount sufficient to add 0.50 per cent organic matter and 0.0037 per cent nitrogen.

4. Soil and cane trash as in treatment 3 with a supplement of 0.0057 per cent nitrogen as ammonium sulphate and 0.013 per cent calcium as the carbonate.

5–8. Treatments similar to 1 to 4, except that they were kept saturated with water, while treatments 1 to 4 were held at optimum moisture.

Distilled water was used in keeping up the moisture supply. The soil was not cropped or allowed to drain.

Table 3.—Reducing capacity, oxidation-reduction potential and concentrations of substances 3 weeks after flooding Sharkey clay loam in 3-gallon pots.

Treatment	Ml. 0.1 N ox. soln. reduced by 10 g. soil	Eh in volts at 31°	pH	Nitrate N p. p. m.	Ammon. N p. p. m.	Soluble Fe p. p. m.	Soluble Mn p. p. m.	Soluble P p. p. m.	Sulfate S p. p. m.	Sulfide S p. p. m.*
1	0.4	0.47	6.7	21.5	2.4	trace	none	1.4	20	0.6
2	0.4	0.46	6.9	26.0	2.7	trace	none	1.6	22	0.5
3	0.2	0.45	6.7	trace	2.5	trace	none	1.9	21	0.0
4	0.4	0.46	6.9	25.5	3.1	trace	none	1.4	63	0.5
5	2.0	0.24	7.0	none	22.3	1.8	2.8	0.4	0	13.0
6	6.0	0.05	7.0	none	54.6	2.4	2.3	0.4	0	10.4
7	4.7	0.06	6.9	none	10.6	2.9	2.9	0.4	0	11.9
8	5.0	0.07	7.0	none	36.7	1.3	2.8	0.4	0	29.9

*Insoluble in water, soluble in dilute hydrochloric acid.

After three weeks the soil under the different treatments was sampled and the various determinations made. The results are given in table 3 on the basis of the dry soil.

The data show that decomposition of organic matter did not cause the accumulation of reduced products or lower the oxidation-reduction potential when the soil was kept at optimum moisture. Decomposition of organic matter under the water-logged conditions increased markedly the amount of reduction in the soil and lowered the Eh to almost the value of the hydrogen electrode. The pH of the soil was increased only slightly as the Eh was lowered. Theoretically, lowering the oxygen pressure should increase the pH (54). An increase in ferrous iron as the hydroxide under the reducing condition would also tend to give a higher pH (31). Although there was an accumulation of soluble iron and manganese, the amounts were lower than expected. Since water soluble sulphides could not be detected, it is possible that the iron and manganese were precipitated largely as sulphides. Nitrates were reduced to ammonia under the water-logged conditions, but nitrites did not accumulate to more than 0.1 p.p.m. The results show that the decomposition of the different forms of fresh organic matter was about equally effective in lowering the oxidation-reduction potential and in increasing the general reducing conditions. The reduction in the check or untreated soil was neither so intense nor of as high capacity as in soil which had been treated with fresh organic matter.

The results given in table 4 show the reducing capacity, the Eh, and the gains or losses in nitrogen in the Sharkey soil, three months after the treatments were applied. It can be seen that the amount of reduction in all the treatments that were water-logged increased with time. The Eh, however, was only slightly lowered as the time following the application of the treatment increased beyond three weeks. The water-logged check was an exception, and the slow rate of fall in the Eh in this treatment which contained no fresh organic matter indicates that the development of a low oxidation-reduction potential is largely dependent on the rapid decomposition of fresh organic matter. The most significant fact shown by the data in table 4 is that there was a small gain in total nitrogen by fixation in the treatments where fresh organic matter was added to the soil and the moisture kept at optimum, but when the soil was water-logged, there was a loss in total nitrogen by reduction or denitrification. However, it is important to note that the soil had to be dried after being sampled wet, and although it was dried as quickly as possible at 40°, there is the possibility that some nitrogen was lost in going from the wet to the dry condition.

Table 4.—Reducing capacity, oxidation-reduction potential and the accumulation of nitrogen in Sharkey clay loam 3 months after flooding.

Treatment Number	Ml. 0.1 N ox. soln. reduced by 10 g. soil	Eh in volts at 31°	pH	Nitrate–N p. p. m.	Ammon.–N p. p. m.	Total N %	N lost or gained %
1	0.5	0.49	6.7	62.0	7.9	0.0800	0.0000
2	0.5	0.49	6.7	97.5	11.1	0.0921	0.0027
3	0.4	0.49	6.7	53.0	8.3	0.0847	0.0010
4	0.5	0.49	6.7	91.5	10.7	0.0935	0.0041
5	6.5	0.07	7.0	none	47.7	0.0760	–0.0040
6	6.8	0.04	7.1	none	73.3	0.0846	–0.0048
7	6.9	0.04	7.0	none	44.4	0.0810	–0.0027
8	7.3	0.04	7.1	none	54.5	0.0858	–0.0046

Table 5 shows the effects of irrigation and cropping over a period of forty years on the chemical changes in the profile of Crowley silt loam. The data indicate that silica and iron oxide have increased in the A horizon of the cultivated soil which has become deflocculated. There has been a marked decrease in nitrogen in the cultivated soil, especially in the A horizon. Apparently the phosphorus lost from the soil has been removed by cropping, since the results show that there has been no downward movement of phosphorus.

Table 5.—Total analyses of virgin Crowley silt loam and of deflocculated Crowley silt loam that had been cultivated for 40 years at the Agricultural Experiment Station at Crowley, Louisiana.

Constituents	Virgin Crowley A	Virgin Crowley B	Virgin Crowley C	Defloc. Crowley A	Defloc. Crowley B
SiO_2	78.50%	75.60%	67.14%	81.14%	77.17%
TiO_2	0.60	0.48	0.48	0.35	0.35
Fe_2O_3	1.70	3.45	4.17	3.13	3.41
Al_2O_3	7.85	11.37	15.63	7.00	9.98
MnO	0.22	0.03	0.06	0.24	0.17
CaO	0.72	0.83	1.13	0.84	0.93
MgO	0.43	0.54	0.79	0.42	0.46
K_2O	0.42	0.41	0.93	0.78	0.79
Na_2O	0.68	1.08	0.73	0.78	0.60
P_2O_5	0.032	0.027	0.031	0.025	0.023
SO_3	0.245	0.245	------	0.193	0.210
Cl	0.00	0.02	0.00	0.01	0.01
Ignition Loss	7.43	5.43	7.45	5.15	5.77
N	0.201	0.111	0.125	0.080	0.081

The results in table 6 show that there has been an increase in the exchangeable bases in the A and B horizons of the cultivated Crowley soil. This has been reported before in work in which the determination of the exchangeable bases had been made by the

ammonium acetate method (18). The pH has also increased in the cultivated soil; while at the same time, the degree of saturation has not increased. The only mechanism that has been suggested for this type of build-up in exchange compounds is the recombination of the acidic and basic groups to form new isoelectric compounds (38). The available phosphorus in the virgin soil is very low and the availability has been further decreased in the cultivated soil. Bartholomew (2) found from studies on changes in the availability of phosphorus in irrigated rice soils, which are similar to the Crowley soil, that the decrease in the availability could be attributed to the high calcium bicarbonate content of the irrigation water. Hibbard's (27) recent review of the factors influencing the fixation of phosphorus indicates that the increase in pH and exchangeable calcium would decrease the available phosphorus. However, the data in tables 3 and 7 indicate that the low availability of phosphorus shown here may have been due to the fixation of phosphorus as an iron phosphate under reducing conditions.

Table 6.—Available nutrients and degree of saturation in virgin Crowley silt loam and deflocculated Crowley silt loam that had been cultivated for 40 years at the Agricultural Experiment Station at Crowley, Louisiana.

	Virgin Crowley A	Virgin Crowley B	Virgin Crowley C	Defloc. Crowley A	Defloc. Crowley B
Total N %	0.201	0.110	0.120	0.080	0.081
Available K, p. p. m.	100	32.5	90.4	61.4	74.0
Available Ca, p. p. m.	820	520	1080	1200	644
Available Mg, p. p. m.	294	325	702	632	516
Available P, p. p. m.					
1:10 soil:acid	1.25	0.75	0.75	0.50	0.50
1:40 soil:acid	3.00	1.60	1.60	1.40	1.40
1:100 soil:acid	12.50	6.00	6.00	4.50	4.50
1:100 soil:H_2O	trace	trace	trace	trace	trace
Exchangeable H					
m. e. per 100 g	9.7	11.4	11.0	9.1	11.2
Total exchange					
m. e. per 100 g.	19.9	22.0	28.9	18.9	21.3
Degree of sat. %	51.2	48.2	61.9	51.9	47.4
pH	6.0	5.8	6.1	7.1	6.1

The effects of reduction on the soluble constituents and yields of rice in the deflocculated Crowley silt loam were obtained by treating 9 kilograms of the soil in 3-gallon pots. The treatments were applied, the soil made up to optimum moisture and the rice planted on December 19. The rice was flooded with distilled water three weeks after germination and kept flooded until mature. It was necessary to move the pots from greenhouse conditions into field conditions on April 21, on which date the samples were taken for the analyses reported in table 7. The treatments applied to the soil were as follows:

1. Check, untreated soil.
2. Soil and 0.50 per cent organic matter in the form of coarsely ground soybean hay.
3. Soil, soybeans and 0.003 per cent P_2O_5 as calcium acid phosphate.
4. Soil, soybeans and 0.006 per cent K_2O as potassium sulphate.
5. Soil, soybeans, P_2O_5 and K_2O.
6. Soil and 0.004 per cent N as ammonium sulphate.
7. Soil, N, and P_2O_5.
8. Soil, N, and K_2O.
9. Soil, N, P_2O_5 and K_2O.

The data show that the soil under the rice was highly reducing and that the treatments which contained the organic matter caused the greatest reduction and accumulation of reduced products. There were large accumulations of soluble iron and manganese in the soil solution. The most noticeable effect associated with the experiment was the formation of an incrustation of iron and manganese oxides on and around the older roots of the rice. This incrustation began to form on the roots about 10 days after flooding. A microscopic examination of freshly cut sections of the roots stained with an acid solution of potassium thiocyanate shows that the iron in the incrustation penetrated the outer layer of cells. Although the addition of the organic matter increased the amount of iron in the soil solution, apparently the tendency is for the iron not to be precipitated on the roots so long as there is an active production of carbon dioxide. There was a relatively small amount of soluble aluminum in the soil solution, and the different treatments seem to have had little or no effect on the soluble aluminum. Extremely small amounts of soluble phosphorus were found, even where phosphorus had been added in the treatment. The decomposition of the fresh organic matter caused a very slight increase in the phosphorus appearing in the soil solution. The amount of soluble silica in the soil was high, but it was not changed greatly by any of the treatments.

Table 7.—Reducing capacity, oxidation-reduction potential and constituents in the soil solution of deflocculated Crowley silt loam which was planted to rice in 3-gallon pots and kept continuously flooded for 3 months.

Treatment	Ml. 0.1 N ox. soln. reduced by 10 g. soil	Eh in volts	pH	Fe p. p. m.	Mn p. p. m.	Al p. p. m.	P p. p. m.	SiO_2 p. p. m.
1	4.0	0.19	7.4	1.2	13.3	0.8	0.02	21
2	6.6	0.09	7.3	15.0	14.3	0.9	0.03	22
3	5.1	0.10	7.3	13.0	8.0	0.9	0.03	21
4	6.7	0.09	7.2	18.0	9.5	0.8	0.03	24
5	4.6	0.15	7.2	26.0	11.1	1.0	0.03	23
6	3.3	0.18	7.4	8.0	-----	1.2	trace	24
7	3.9	0.17	7.5	10.9	-----	0.9	0.02	25
8	3.4	0.20	7.8	4.6	-----	1.1	trace	30
9	2.9	0.19	7.2	8.0	-----	1.0	trace	24

In the effects of the various treatments given above on the yields of rice it was very obvious that the treatment of soybeans P_2O_5, and K_2O gave the greatest increase, which was 136 per cent more than the yield of the check. The addition of soybeans and P_2O_5 increased the yield 118 per cent; soybeans and K_2O gave an increase of 92 per cent. None of the treatments which did not contain organic matter produced significant increases. Apparently, the presence and decomposition of the organic matter had a most marked effect on the flocculation of the soil. The root development in the pots containing the organic treatments was much greater, and the roots were much less coated by the iron incrustations.

In the progress of the work, it had become apparent that the decomposition of fresh organic matter in a water-logged soil is the most important factor affecting the intensity and amount of reduction. To test the effect of the soil organic matter in a sample of the deflocculated Crowley soil from which a crop of rice had just been removed in comparison with fresh organic matter which was added to the same soil, treatments of coarsely ground soybean hay, gypsum and sulphur were added, in the amounts indicated in table 8, to 500-gram portions of the soil in 1-liter beakers. The soil was submerged to a depth of four inches with distilled water and kept submerged at a constant temperature of 30° for one month. The Eh was determined daily. The data indicate that the rate of decomposition of soil organic matter in a deflocculated soil which had just been cropped under irrigated conditions and to which no fresh organic matter had been added was too slow to lower the Eh more than 0.13 of a volt within a month. The reducing intensity in the soil without fresh organic matter was too low to effect reduction of sulphates. In the soil to which fresh organic matter was added the maximum intensity of reduction developed within 19 days and sulphides accumulated after the Eh was lowered beyond 0.34. The pH

in the above treatments varied from 7.0 to 7.2. This variation in the pH was not considered of any significance in interpreting the results. The results given in table 8 suggest that the use of the oxidation-reduction potential in following the course of reduction in a soil is only of general value. The virgin Crowley silt loam in a well drained state has an Eh of 0.53. After the soil has been irrigated for a number of years and then aerated and dried, the Eh is 0.67. Evidently there is some system such as the inorganic iron system, which increases under the conditions of wetting and drying, that imposes a higher potential in the irrigated soil when it is dried than existed in the normal virgin soil under the same degree of aeration.

Table 8.—Changes in the oxidation-reduction potential in the surface 3 inches of Crowley silt loam kept under 4 inches of water for 30 days at 30° Centigrade.

Days of submergence	Eh in volts				
	Soil alone (check)	Soil + 0.5% O. M.	Soil + O. M. .18% $CaSO_4$	Soil + O. M. .04% S	Soil + .18% $CaSO_4$
0	0.67	0.67	0.67	0.67	-----
1	0.66	0.44	0.63	0.48	-----
3	0.66	0.19*	0.36*	0.34*	-----
4	0.66	0.14	0.17	0.22	-----
5	0.66	0.12	0.14	0.14	-----
6	0.65	0.13	0.13	0.12	-----
7	0.65	0.12	0.13	0.12	-----
8	0.64	0.12	0.12	0.12	-----
10	0.64	0.10	0.10	0.10	-----
11	0.63	0.11	0.10	0.10	-----
12	0.61	0.10	0.11	0.11	-----
13	0.61	0.10	0.10	0.10	-----
14	0.60	0.11	0.11	0.10	-----
15	0.61	0.10	0.09	0.10	-----
17	0.55	0.10	0.09	0.10	0.52**
18	0.54	0.10	0.10	0.10	0.51
19	0.55	0.09	0.09	0.09	0.49
20	0.55	0.09	0.09	0.09	0.50
21	0.54	0.09	0.09	0.09	0.50
22	0.54	0.09	0.09	0.09	0.49
24	0.54	0.09	0.09	0.09	0.49
25	0.54	0.09	0.09	0.09	0.48
26	-----	-----	-----	-----	0.48
27	-----	-----	-----	-----	0.48
28	-----	-----	-----	-----	0.47
29	-----	-----	-----	-----	0.47
30	-----	-----	-----	-----	0.47

*From this point on, tests indicated that hydrogen sulfide was present.
**This treatment was started late.

Observations made in studying the profile of the deflocculated Crowley soil and results from chemical analyses indicated that some practical method for flocculating the soil and decreasing the alkalinity needed to be devised. Seven-kilogram portions of the soil were placed in 8-liter pyrex percolators which had been set into a

fixed housing so that only the tops of the percolators were exposed to the weather. The bottoms of the percolators were fitted with perforated porcelain plates and an inch layer of acid-washed sand was placed on top of the plates. Traps which would not allow air to enter the percolators from the bottom were fitted to the outlets. Large receiving bottles were then connected through the trap tubes to outlets of the percolators. In effect the set-up was equivalent to a set of small lysimeters. The treated soil was placed in the lysimeters on May 21. The soil was made up to optimum moisture and allowed to stand until June 1, when it was set to rice plants which were six inches high at the time of transplanting. The soil was flooded immediately and was kept flooded, except at the time of harvesting, for over a year. These lysimeters, as well as all the pots described in the following experiments, were exposed to the weather in the field and distilled water was added to supply the water not furnished by the rainfall. The treatments were kept submerged to a depth of four inches. The treatments consisted of the application of organic matter as coarsely ground soybean hay, gypsum, lime as calcium carbonate, and sulphur as powdered sulphur. The amounts and combinations of the different materials are indicated in table 9, which also shows the effects of the treatments on the yield of rice. The data show organic matter alone proved the most beneficial of the single treatments. Somewhat higher yields were secured with organic matter and gypsum and from organic matter, sulphur and lime, but an inspection of the roots of the rice showed that where sulphur or gypsum had been applied there were heavy deposits of black sulphides on the rice roots. In the treatments where either the sulphur or gypsum was added without organic matter the yields were reduced. The application of sulphur or gypsum to the soil immediately before planting rice in soil where the sulphates cannot drain out of the soil is very harmful to rice, due to the fact that the sulphates will be reduced to sulphides which may be toxic to rice at high accumulations.

Table 9.—Effects of treatments on yield of rice in deflocculated Crowley silt loam in 8-liter lysimeters.

	Treatment	Yield of grain in grams per lysimeter	% gain or loss
1	Check, no treatment	5.2	0.0
2	0.80% organic matter	11.9	127.8
3	0.198% $CaSO_4.2H_2O$	2.3	− 51.7
4	0.12% $CaCO_3$	4.8	− 7.7
5	0.04% S and .12% $CaCO_3$	3.5	− 32.7
6	0.04% S	2.8	− 46.2
7	0.198% $CaSO_4$ and .80% organic matter	12.5	140.5
8	0.12% $CaCO_3$ and .80% organic matter	10.8	106.7
9	0.04% S and .80% organic matter	10.3	98.2
10	0.04% S and .80% organic matter and .12% $CaCO_3$	12.4	137.9

Table 10.—Effects of treatments on the rate of percolation at different intervals after flooding in deflocculated Crowley silt loam which had been placed in 8-liter lysimeters and cropped to rice.

Treatment	Percolation in c.c. per hour at intervals after flooding								
	6 days	8 days	15 days	22 days	29 days	36 days	43 days	54 days	13 months*
1	0.0	------	------	------	------	----	----	----	3.5
2	0.0	------	5.1	------	------	----	----	0.9	10.0
3	0.0	------	------	------	2.6	----	----	1.4	8.5
4	0.0	------	5.1	------	------	----	----	2.3	10.0
5	2.4	------	6.5	------	5.9	----	6.0	4.2	70.0
6	0.0	------	------	------	------	----	----	1.1	24.0
7	29.4	23.8	31.0	21.2	13.0	5.0	2.2	---	29.5
8	27.5	27.3	30.0	21.2	12.0	5.0	2.2	----	34.0
9	15.8	------	6.8	------	------	----	----	0.5	124.0
10	40.2	38.0	55.0	34.5	8.3	3.7	0.0	----	53.5

*Readings taken 9 months after harvesting the rice crop during which period the lysimeters had not been allowed to drain and the soil was kept saturated and fallow.

In studying the effects of adding organic matter, gypsum, lime, and sulphur on the rate of percolation in the deflocculated soil, the treatments and lysimeters were the same as given with the data in table 9. The rate of percolation was determined at the intervals indicated in table 10. The depth of the column of soil in the lysimeters was 15 inches. On account of the use of a short column of soil, which allowed too much percolation, the percolation had to be interrupted. The rates given were determined from the amount of percolation for the day preceding the date of the reading. The data show that within the first month after flooding the treatments of organic matter with lime and sulphur, organic matter with gypsum, and organic matter with sulphur were very effective in increasing the rate of percolation. There was no percolation in the check during the first two months of the experiment. After the rice crop began to head, the percolation in all the treatments reached minimum values. This was probably due partly to the absorption of water by the roots in the lower part of the column of soil. The lysimeters were not allowed to drain for 9 months after the rice crop was harvested. Then, the rate of percolation was determined over a period of a week, and it was found, as shown in table 10, that organic matter with sulphur, sulphur with lime, and organic matter with sulphur and lime were the most effective treatments used for increasing the rate of percolation. There was some percolation in the check at this time, which indicated that root channels left from the rice crop were partly effective in increasing the percolation.

Analyses were made at various dates on the percolate from the soil in the lysimeters. The effect of the treatments on exchangeable sodium was of special interest, since it had been found that the soil contained 1.25 milligram equivalents of exchangeable sodium. The buffer curve of the soil indicated that the amount of sulphur used in the experiment should be sufficient to change the reaction of the soil to pH 6.5, which was considered to be optimum, and to remove most of the exchangeable sodium. The results given in table 11 show that the percolation from the gypsum and sulphur treatments contained large amounts of soluble sodium. However, the other treatments affected the solution of sodium in about the same amounts. In general, the data show that large amounts of sodium, silica, iron, and manganese came into solution from the influence of flooding. There was no phosphorus in the percolate within the first two weeks after flooding, and only small amounts appeared at later dates. Small amounts of aluminum were found in the percolate. The different rates of drainage and the fact that the drainage was interrupted will not allow an accurate comparison of the percolation losses under the different treatments to be made.

Table 11.—Soluble constituents in the percolate from deflocculated Crowley silt loam which had been placed in 8-liter lysimeters.

Treatment	Date	Ca p. p. m.	Na p. p. m.	Fe p. p. m.	Mn p. p. m.	Al p. p. m.	SiO_2 p. p. m.	P p. p. m.	Total salts p. p. m.
1		No percolate							
2	6—22	5	67	2.0	2	0.02	64	0.00	953
	8— 1	293	162	116.0	30	0.06	117	0.00	1315
3	7— 6	125	28	trace	8	0.01	61	0.00	800
	8— 1	167	160	0.4	6	0.09	64	0.33	3100
4	6—22	5	76	0.1	2	0.21	38	0.00	412
	8— 1	72	168	0.4	0	0.21	28	0.39	666
5	6—13	62	18	2.0	7	0.38	55	0.00	460
	8— 1	162	176	0.7	0	0.76	23	0.30	1200
6	8— 1	180	136	2.8	38	0.55	138	0.00	1416
7	6—13	21	22	3.1	4	0.00	66	0.00	380
	7—13	480	175	8.0	25	0.00	37	0.00	3800
8	6—13	trace	40	1.0	2	0.01	65	0.00	400
	7—13	210	170	9.0	8	0.01	40	0.11	1820
9	6—13	6	55	12.0	8	0.23	64	0.00	450
	8— 1	244	170	20.0	25	0.23	70	0.00	1860
10	6—13	trace	28	3.0	4	0.00	66	0.00	340
	7—13	240	160	7.0	7	0.00	30	0.10	1330

The relationship of intermittent drainage through the growing season to the effectiveness of organic matter and a complete fertilizer in promoting the growth of rice was studied in virgin Crowley silt loam and in deflocculated Crowley silt loam in 3-gallon pots. The soil was treated in 10-kilogram portions with organic matter and a complete commercial fertilizer. The organic matter consisted of coarsely ground soybean hay. The commercial fertilizer was an 8-8-8 mixture of ammonium sulphate, superphosphate, and muriate of potash. The fertilizer and organic matter were added singly and in combinations. The treatments were applied on April 28. Rice was planted in the pots on May 19, and on June 6 the pots were flooded with distilled water. The pots were kept in the field and exposed to the rain. Two series of the treatments on each soil were run. In one series the soil was kept flooded continuously. In the other series the pots were drained at 3-week intervals during the growing season. The treatments and their effect on the yield of rice are shown by the data in table 12. In the deflocculated soil which was drained intermittently, organic matter increased the yield 70 per cent, while the 8-8-8 fertilizer gave no increase in yield. When the deflocculated soil was flooded continuously to a depth of four inches, the organic matter gave only a 35 per cent increase, and the fertilizer raised the yield 45 per cent. Organic matter and fertilizer, when used together, were very effective under conditions of both intermittent and continuous flooding. The increases in yields were 87 and

Table 12.—Effects of treatment and intermittent drainage on yield of rice in virgin Crowley silt loam and in deflocculated Crowley silt loam in 3-gallon pots.

Treatment	Yield of grain in grams per pot	% gain or loss
Virgin soil drained every three weeks		
Check, no treatment	25.3	0.0
0.50% organic matter	29.4	16.3
600# per acre of an 8-8-8	30.0	18.7
0.50% O. M. and 600# per acre of an 8-8-8	31.9	26.2
Virgin soil flooded continuously		
Check, no treatment	21.9	0.0
0.50% organic matter	27.3	24.5
600# per acre of an 8-8-8	24.2	10.5
0.50% O. M. and 600# per acre of an 8-8-8	25.9	18.3
Deflocculated soil drained every three weeks		
Check, no treatment	9.4	0.0
0.50% organic matter	16.00	70.2
600# per acre of an 8-8-8	8.7	– 7.4
0.50% O. M. and 600# per acre of an 8-8-8	17.6	87.2
Deflocculated soil flooded continuously		
Check, no treatment	9.2	0.0
0.50% organic matter	12.4	35.0
600# per acre of an 8-8-8	13.3	44.8
0.50% O. M. and 600# per acre of an 8-8-8	17.8	93.9

94 per cent respectively. The intermittent drainage had no significant effect on the check or on the untreated deflocculated soil. Intermittent drainage increased the yields from all the treatments in the virgin soil. The increases varied from 12 to 22 per cent above the yields of the corresponding treatments in the continuously flooded virgin soil. Apparently, drainage during the growing period of rice is beneficial in a soil well supplied with active organic matter where large amounts of sulphides and soluble reduced iron and manganese may accumulate, but in a deflocculated soil which is low in organic matter and low in the available nutrients, especially nitrogen, the benefits from the removal of reduced products do not more than compensate for loss of water and nutrients through extra drainage. There were growths of algae in all the pots in the experiment and it is not known to what extent the algae may have influenced the aeration of the virgin soil. Apparently they did not influence, to any great extent, the aeration of the deflocculated soil, which had received no addition of organic matter.

DISCUSSION

The data in tables 3, 4, 7, and 8 show that the development of reducing conditions is relatively slow where the soil contains no fresh organic matter. The activity of the soil organic matter in the Sharkey soil was much greater than that of the soil organic matter in the deflocculated Crowley soil. The untreated Sharkey soil after flooding finally developed an Eh 0.07 as compared with Eh 0.04, where the soil had received fresh organic matter. In the Crowley soil to which no fresh organic matter was added, the Eh did not drop below 0.47, but in the presence of fresh organic matter the Eh was lowered from 0.63 to 0.09 within 19 days. Apparently, the development of reducing conditions depends on the rapid removal of oxygen from the soil air or from oxides in the soil. The diffusion of oxygen from the layer of water on top of the soil is too slow to be effective in maintaining any appreciable amount of oxidation in the soil. A considerable downward movement of water through the soil would be much more effective in supplying oxygen.

The accumulation of reduced products in the soil, as shown by the direct determination of sulphides and soluble iron and manganese and as shown by determination of the amount of 0.1 N potassium dichromate that a definite quantity of the soil would reduce, when compared with the changes in the Eh, shows that, in general, an inverse relationship exists between the reducing capacity and Eh. Data in tables 3 and 4 show, however, that at low Eh values there may be a relatively great increase in the amount of reduction in the soil, with little or no decrease in the oxidation-reduction potential. It was found also that there is apparently no difinite relationship between the amount of soluble iron and manganese and the total

reducing capacity of the soil. The inorganic colloids probably effect changes in the oxidizing solution, and they may also effect changes in the Eh.

In determining the oxidation-reduction potentials in water-logged soils, difficulty was experienced in reading the potentiometer due to a rapid negative drift. The problem of sampling presented a great many difficulties. Variations of depth in sampling will be reflected by variations in the potential. Any manipulation which exposes the wet soil to air tends to raise the Eh. Contrary to what had been expected from the review of literature, the pH of the soil varied only slightly with the relatively large changes in Eh.

One of the most important observations made during the course of the work was that, although the addition of organic matter to the soils which were flooded markedly increased the intensity of reduction and the accumulation of soluble reduced iron and manganese, the organic matter greatly increased the yield of rice. Apparently rice is highly tolerant to soluble iron and manganese and extremely low concentrations of oxygen in the soil, as shown by the low Eh values found under the water-logged conditions. The mechanism by which decaying organic matter increases the tolerance of rice to soluble iron and manganese was not determined, but it appeared that the effect was largely through the increase of the availability of phosphorus and nitrogen and through the prevention of the precipitation of iron compounds on the roots of the rice. Apparently in a deflocculated soil where production of carbon dioxide is low and the diffusion of gases very slow, there is enough oxygen diffusing from the roots of the rice plants to cause the precipitation of oxides of iron and manganese at the root surfaces.

The data in tables 3 and 7 show that water-logging reduces the solubility of phosphorus and that the addition of organic matter to the soil tends to increase the solubility of the phosphorus.

SUMMARY AND CONCLUSIONS

The effects of water-logging and the decomposition of organic matter on the development of reducing conditions in typical rice soils have been determined and methods for improving the permeability of deflocculated soils and increasing the yield of rice on such soils have been suggested.

Development of a low oxidation-reduction potential in a water-logged soil is largely dependent on the decomposition of active organic matter in the soil. The addition of fresh organic matter to submerged soils causes a rapid lowering of the Eh. In the cases observed, where the fresh organic matter was added, the greatest intensity of reduction was developed within approximately the first three weeks, following the submergence of the soil. The lowest

oxidation-reduction potentials observed varied from Eh 0.04 to 0.09. It was definitely shown in a soil in which the organic matter had been previously depleted by cropping to rice that the Eh was only lowered from 0.67 to 0.47 by water-logging in the absence of active organic matter.

In general, the oxidizing intensity as shown by Eh values and the accumulation of reduced products in the soil are inversely related, but neither can be used as an index of the ability of a submerged soil to produce rice.

Rice plants growing in a flooded soil will tolerate the presence of large amounts of soluble iron and manganese if the soil is well supplied with actively decomposing organic matter. In the absence of easily decomposable organic matter in a deflocculated soil, large amounts of iron compounds were found to be precipitated on and around the older roots of the rice plants. Presumably, this is due to the low production of carbon dioxide in the soil and to the excretion or diffusion of oxygen from the roots.

It was found that flooding the soil caused small losses of soil nitrogen by denitrification.

The solubility of phosphorus was found to be markedly lowered from the effects of the development of reducing conditions in the soil.

Applications of sulphur and gypsum in various combinations were found to be effective in increasing the permeability of deflocculated soil. However, the indications are that it would not be advisable to apply either sulphur or gypsum immediately before planting a crop of rice, for sulphides would tend to be formed in the soil after irrigation. Under the conditions where sulphides were found in the largest amounts, precipitates of sulphides occurred on the roots and reduced the yields of rice.

The application of leguminous organic matter was found to increase the yield of rice in a deflocculated soil. The use of commercial fertilizers without the addition of organic matter was not effective.

LITERATURE CITED

1. Allyn, W. P., and Baldwin, I. L. Oxidation-reduction potentials in relation to the growth of an aerobic form of bacteria Jour. Bact. 23:369-398. 1932.

2. Bartholomew, R. P. Changes in the availability of phosphorus in irrigated rice soils. Soil Sci. 31:209-218. 1931.

3. Bonazzi, A. Estudios sobre fisiologia del arroz. Memorias de la Sociedad Cubana de Historia Natural 8:169-200. 1934.

4. Bradfield, R., Batjer, L. P., and Oskamp, J. Soils in relation to fruit growing in New York: IV. The significance of the oxidation-reduction potential in evaluating soils for orchard purposes. N. Y. (Cornell) Agr. Exp. Sta. Bul. 592. 1934.

5. Breazeale, J. F. The absorption of carbon by the roots of plants Jour. Agr. Res. 26:303-311. 1923.

6. Brenchley, W. E. Inorganic plant poisons and stimulants. pp. 84-107. Cambridge University Press, London. 1927.

7. Brown, L. A. Oxidation-reduction potentials in soils: I. Principles and electrometric determination. Soil Sci. 37:65-76. 1934.

8. Buckingham, E. Contributions to our knowledge of the aeration of soils. U. S. Dept. Agr. Bur. Soils Bul. 25. 1904.

9. Buehrer, T. F. The movement of gases through the soil as a criterion of soil structure. Ariz. Agr. Exp. Sta. Tech. Bul. 39. 1932.

10. Buehrer, T. F. The physico-chemical relationships of soil phosphates. Ariz. Agr. Exp. Sta. Tech. Bul. 42. 1932.

11. Burd, J. S., and Martin, J. C. Secular and seasonal changes in the soil solution. Soil Sci. 18:151-167. 1924.

12. Burgess, P. S. The soil solution extracted by Lipman's direct pressure method compared with 1:5 water extracts. Soil Sci. 14:191-215. 1922.

13. Cannan, R. K., Cohen, B., and Clark, W. M. Studies on oxidation-reduction: X. Reduction potentials in cell suspensions. U. S. Hyg. Lab. Bul. 151. 1928.

14. Cannon, W. A. Physiological features of roots with especial reference to the relation of roots to aeration of the soil. pp. 119-122. Carnegie Institution, Washington. Pub. 368. 1925.

15. Clark, W. M. Recent studies on reversible oxidation-reduction in organic systems. Chemical Reviews 2:127-178. 1925.

16. Conner, S. D. Soil acidity as affected by moisture conditions of the soil. Jour. Agr. Res. 15:321-329. 1918.

17. Copeland, E. B. Rice. pp. 58-59. Macmillan and Co., Ltd., London. 1924.

18. Fieger, E. A., and Sturgis, M. B. Profile studies of the coastal prairie soils of Louisiana: I. Exchange and solution properties. Soil Sci. 38:267-277. 1934.

19. Fraps, G. S. Relation of the water-soluble potash, the replaceable, and acid soluble potash to the potash removed by crops in pot experiments. Tex. Agr. Exp. Sta. Bul. 391. 1929.

20. Fraps, G. S. Possibilities of sulphur as a soil amendment. Tex. Agr. Exp. Sta. Bul. 414. 1930.

21. Gedroiz, K. K. Exchangeable cations of the soil and the plant:

I. Relation of plant to certain cations fully saturating the soil exchange capacity. Soil Sci. 32: 51-63. 1931.

22. Gillispie, L. J. Reduction potentials of bacterial cultures and of water-logged soils. Soil Sci. 9:199-216. 1920.

23. Halvorson H. O. Studies on the transformations of iron in nature: III. The effect of CO_2 on the equilibrium in iron solutions. Soil Sci. 32:141-164. 1931.

24. Harrison, W. H., and Aiyer, S. The gases of swamp rice soils: I. Their composition and relation to the crop. India. Dept. Agr., Mem. Chem. Ser. 3:65-106. 1913.

25. Harrison, W. H., and Aiyer, S. The gases of swamp rice soils: II. Their utilization for the aeration of the crop. India Dept. Agr., Mem. Chem. Ser. 4:1-17. 1914.

26. Harrison, W. H. The gases of swamp rice soils: VI. Carbon dioxide and hydrogen in relation to rice soils. India. Dept. Agr., Mem. Chem. Ser. 5:181-194. 1920.

27. Hibbard, P. L. Factors influencing phosphate fixation in soils. Soil Sci. 39:337-358. 1935.

28. Hilgard, E. W. Geological reconnoissance of the state of Louisiana. pp. 13-15 New Orleans Academy of Sciences. 1873.

29. Hissink, D. J. Method for estimating adsorbed bases in soils and the importance of these bases in soil economy. Soil Sci. 15:269-276. 1923.

30. Joffe, J. S., and McLean, H. C. The availability of replaceable cations. Proc. First Internat. Cong. Soil Sci. 2:256-263. 1927.

31. Joffe, J. S. Soil profile studies: VII The glei process. Soil Sci. 39:391-402. 1935.

32. Jones, J. W. Effect of reduced oxygen pressure on rice germination. Jour. Amer. Soc. Agron. 25:69-81. 1933.

33. Kapp, L. C. Study of rice fertilization. Ark. Agr. Exp. Sta. Bul. 291. 1933.

34. Keen, B. A. The physical properties of the soil. pp. 343-354. Longmans, Green and Co., London. 1931.

35. Kohnke, H., and Bradfield, R. Factors affecting the redox potential of soils. Amer. Soil Survey Asso. Bul. 16. 1935.

36. Leather, J. W. Soil gases. India. Dept. Agr., Mem. Chem. Ser. 4:85-134. 1915.

37. Lemmermann, O. Methoden für die Untersuchung des Bodens. II. pp. 41-42 Verlag Chemie, Berlin. 1934.

38. Mattson, S., and Hester, J. B. The laws of soil colloidal behavior: XV. The degradation and regeneration of the soil complex. Soil Sci. 39:75-84. 1935.

39. McGeorge, W. T. Iron aluminum and manganese in the soil solution of Hawaiian soils. Soil Sci. 18:1-12. 1924.

40. McGeorge, W. T. Phosphate availability in alkaline calcareous soils. Jour. Amer. Soc. Agron. 25:351-354. 1933.

41. Piper, C. S. The availability of manganese in the soil. Agr. Sci. 21:762-779. 1931.

42. Reed, J. F., and Sturgis, M. B. Chemical method for classifying the soils of Louisiana as to their ability to furnish the nutrient elements and as to their degree of base saturation. Unpublished data. La. Agr. Exp. Sta. 1935.

43. Remezov, N. P. Dynamics of the oxidation-reduction potential in podzolized soils. 1930. Original not seen. Abstracted in Proc. Internatl. Soc. Soil Sci. 7:136-137. 1932.

44. Robinson, W. O. Method and procedure of soil analysis used in the Division of Soil Chemistry and Physics. U. S. Dept. Agr. Cir. 139. 1930.

45. Robinson, W. O. Some chemical phases of submerged soil conditions. Soil Sci. 30:197-218. 1930.

46. Russell, E. J. Soil conditions and plant growth. pp. 367-370. Longmans, Green and Co., London. 1932.

47. Schreiner, O., and Failyer, G. H. Colorimetric, turbidity, and titration methods used in soil investigations. U. S. Bur. Soils Bul. 31. 1906.

48. Smith, F. B., and Brown, P. E. The diffusion of carbon dioxide through soils. Soil Sci. 35:413-421. 1933.

49. Smith, F. B., and Brown, P. E. The concentration of carbon dioxide in the soil air under various crops and in fallow soils. Ia. State Coll. Jour. Sci. 8:1-16. 1933.

50. Sturgis, M. B. The effect of additions of nitrogen on the decomposition of sugarcane trash. Jour. Amer. Soc. Agron. 24:690-706. 1932.

51. Sturgis, M. B. Review of experimental results on fertilizers for rice. Mimeographed Bul. La. Agr. Exp. Sta. 1934.

52. Walker, R. H., Firkins, B. J., and Brown, P. E. The measurement of the degree of saturation of soils with bases. Ia. Agr. Exp. Sta. Res. Bul. 139. 1931.

53. Willis, L. G. Oxidation-reduction potentials and the hydrogen-ion concentration of a soil. Jour. Agr. Res. 45:571-575. 1932.

54. Willis, L. G. Some potential changes induced by liming suspensions of a peat soil. N. C. Agr. Exp. Sta. Tech. Bul. 47. 1934.

ACKNOWLEDGMENTS

The author expresses his sincere appreciation to Dr. F. B. Smith, under whose direction this work was done. Particular acknowledgment is made to Mr. J. F. Reed, who helped take care of the experiments at times when the author was called to unavoidable routine. With the approval and encouragement of Dr. C. T. Dowell and Dr. H. B. Brown this work was made possible.

PIKE BURDEN, INC.